STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 3, 2009

COMPARATIVE STUDY OF CARBON PASTE ELECTRODES MODIFIED WITH METHYLENE BLUE AND METHYLENE GREEN ADSORBED ON ZEOLITE AS AMPEROMETRIC SENSORS FOR H_2O_2 DETECTION

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ABSTRACT. Methylene Blue (MB) and Methylene Green (MG) adsorbed on a synthetic zeolite (13X) and incorporated in carbon paste resulted in modified electrodes (MB-13X-CPEs and MG-13X-CPEs) with electrocatalytic activity for H_2O_2 reduction. Using the treatment proposed by Laviron, the heterogeneous electron transfer rate constant (k_s) was estimated, and values between 2.9 and 6.6 s^{-1} were found. The electrocatalytic ability of the modified electrodes towards H_2O_2 electroreduction depends mainly on the formal potential of mediator. The MB-13X-CPEs and MG-13X-CPEs respond to H_2O_2 in the linear range from $\sim 10^{-4}$ to 10^{-1} M. The best performances were attained with MB-13X-CPEs in phosphate buffer (pH 6): detection limit 0.13 mM, at a signal to noise ratio equal to 3; sensitivity 0.94 mA/M, calculated as the ratio I_{max}/K_M.

Keywords: *carbon paste electrodes; Methylene Blue; Methylene Green; Zeolite; Hydrogen peroxide.*

INTRODUCTION

Zeolites ability to immobilize large amounts of redox dyes, with significant solubility in specific experimental conditions recommend them as attractive matrices for the preparation of composite electrode materials [1-4]. Methylene Blue (MB) and Methylene Green (MG) are water-soluble cationic dyes with the redox potential close to the optimal potential window for amperometric detection of ascorbic acid, NADH or H_2O_2. Electrodes incorporating zeolites modified with MB and MG were realized for amperometric detection of ascorbic acid [2,5,6], NADH [5,7] or H_2O_2 [8-11].

Continuing our preoccupation in obtaining modified electrodes by immobilization of different dyes onto zeolites [6,7,9-11], in the present paper, the electrochemical behavior and the electrocatalytic properties of carbon paste

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electrodes incorporating a synthetic zeolite (molecular sieves 13X, Aldrich) modified with Methylene Blue (MB-13X-CPEs) or Methylene Green (MG-13X-CPEs) are assessed comparatively and the influence of some experimental parameters (pH, and potential scan rate) on the voltammetric response of these electrodes were investigated.

The electrochemical parameters for the heterogeneous electron transfer process corresponding to the surface immobilized mediators were determined from voltammetric measurements. All observed differences were used to put on evidence the influence of the mediator structure on the redox response. The modified electrodes were tested for electrocatalytic mediated reduction of H_2O_2 at MB-13X-CPES and MG-13X-CPEs, using cyclic voltammetry (CV) and the calibration of modified electrodes were realized by using amperometry.

RESULTS AND DISCUSSION

Cyclic voltammetric experiments were carried out using MB-13X-CPEs and MG-13X-CPEs. In Figures 1A and 1B, a pair of well-defined redox waves in the case of both electrodes, can be observed. This peak pair was assigned to the oxidation and reduction of MB and MG adsorbed on the 13X zeolite.

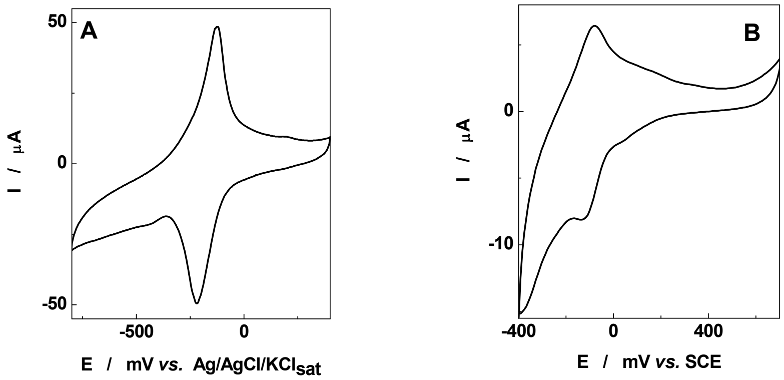


Figure 1. Cyclic voltammograms for MB-13X-CPEs (A) and MG-13X-CPEs (B). Experimental conditions: starting potential, -650 mV *vs.* Ag|AgCl/KCl$_{sat}$ (A) and -400 mV *vs.* SCE (B); potential scan rate, 10 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.

$E^{0'}$ value for MG-13X-CPEs is more positive (see Table 1) than the $E^{0'}$ value for MB-13X-CPEs, suggesting that MG is more difficult to oxidize than MB. This behavior could be explained by the presence of a nitro-group at the 4-position, in the MG structure. The nitro-group is a strong electron acceptor group and it enhances the stability of the compound, making its oxidation more difficult.

Table 1. Electrochemical parameters corresponding to MB-13X-CPEs and MG-13X-CPEs modified electrodes. Experimental conditions: as in Figure 1.

Electrode	E_{pa} *	E_{pc} *	$E^{0'*}$	ΔE_p	Γ (mol cm^{-2})
MB-13X-CPEs	-130	-220	-175	90	$1.40 \cdot 10^{-8}$
MG-13X-CPEs	-35	-81	-58	46	$1.03 \cdot 10^{-8}$

* mV *vs*. Ag|AgCl/KCl$_{sat}$

The peak separation ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) for MB-13X-CPEs and MG-13X-CPEs was found to be 90 mV and 46 mV, respectively, in phosphate buffer, pH 7 (10 mV s^{-1}), indicating a quasi-reversible redox process. The peaks split are larger than that reported for MG adsorbed on graphite (~ 20 mV) [12], indicating a diffusion behavior of the mediator.

As can be observed from Figure 2, for MG-13X-CPEs, the slope of $E^{0'}$ *vs.* pH dependence (pH 4-7) was 0.034 V/pH, indicating a e^-/H^+ ratio equal to 2 corresponding to the reaction:

$$MGH \rightarrow MG^+ + 2e^- + H^+.$$

The $E^{0'}$ *vs.* pH dependence could be mainly explained by the steric impediments which hinder the entrance of the MG molecules in the channels and pores of the zeolite and make them sensitive to the external solution pH change.

Contrarily, for MB-13X-CPEs, $E^{0'}$ does not change significantly with pH. This result is remarkable and can be due to the absence of NO_2 group from MB structure. Due to its smaller size, MB is entrapped in the holes of the 13X type zeolite (host matrix) where it is strongly hold by electrostatic interactions being not affected by the external solution pH change [11].

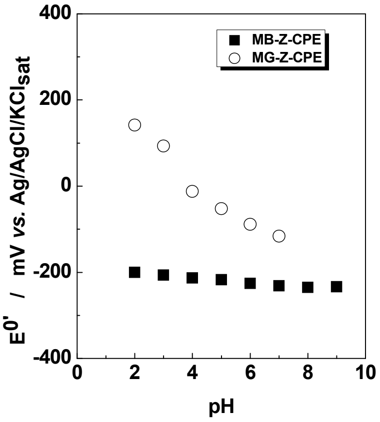


Figure 2. Variation of $E^{0'}$ with pH for MB-13X-CPEs and MG-13X-CPEs. Experimental conditions: potential scan rate, 50 mV s^{-1}; for other conditions, see Figure 1.

Moreover, the slope of the log I -log v dependence (see Table 2) confirms that MB is stronger adsorbed than MG on the zeolite surface.

Table 2. Parameters of the log-log linear regression corresponding to the peak current dependence on the potential scan rate for MB-13X-CPEs and MG-13X-CPEs. Experimental conditions: as in Figure 3.

Electrode	pH	Slope		R / N	
		oxidation	reduction	oxidation	reduction
MB-13X-CPEs	3	0.80	0.92	0.992 / 12	0.996 / 12
	5	0.81	0.95	0.999 / 12	0.997 / 12
	6	0.82	0.96	0.999 / 12	0.997 / 12
	7	0.82	0.95	0.998 / 12	0.995 / 12
	8	0.78	1.01	0.999 / 8	0.998 / 8
	9	0.81	0.96	0.999 / 12	0.998 / 12
MG-13X-CPEs	5	0.67	0.64	0.996 / 11	0.996 / 11
	6	0.62	0.73	0.997 / 12	0.984 / 9
	7	0.57	0.60	0.998 / 10	0.993 / 8

Using the treatment proposed by Laviron [13], the heterogeneous electron transfer rate constant (k_s) and the transfer coefficients (α) were determined (Figure 3 and Table 3). At pH values greater than 5, MB-13X-CPEs present relatively higher k_s values than MG-13X-CPEs, but the differences are not important. The k_s values in the case of MB-13X-CPEs and MG-13X-CPEs are in accordance with the better adsorption of MB and MG on the zeolite and suggest a faster electron transfer rate. It should be mentioned that the values of k_s calculated for MG-13X-CPEs are higher than those obtained using a NaX type synthetic zeolite from Bayer [10], suggesting a stronger interaction between MG and 13X type zeolite than between MG and NaX type zeolite. This confirms that the type of adsorbent is very important for the modified electrode electrochemical behavior.

The differences occurring between the transfer coefficients values, α, corresponding to the two electrodes suggest a different electron transfer mechanism in the two cases and a possible change of the reaction path with increasing pH. Probably, in the case of MB-13X-CPEs the charges are transferred mainly *via* a mechanism involving an ion exchange process between the immobilized positively charged MB species and the supporting electrolyte cations, followed by an electron transfer process occurring between the free MB species and the graphite particles from the carbon paste, while in the case of a MG-13X-CPEs the charge transfer mechanism is partially based on a surface-mediated electron transfer. Moreover, the α values indicate that the redox processes are not fully reversible.

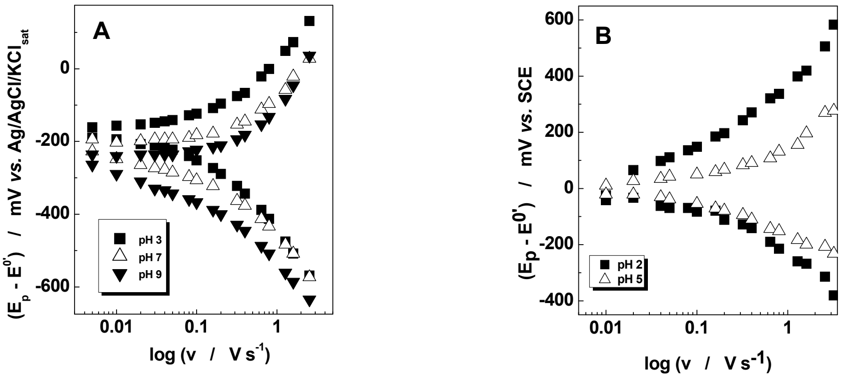


Figure 3. Experimental dependence of (E_p - $E^{0'}$) *vs.* logarithm of the scan rate for MB-13X-CPEs (A) and MG-13X-CPEs (B). Experimental conditions: as in Figure 1.

Table 3. Kinetic parameters for the heterogeneous electron transfer at MB-13X-CPEs and MG-13X-CPEs modified electrodes. Experimental conditions: as in Figure 3.

Electrode	pH	k_s (s^{-1})	α	R/N	
				oxidation	reduction
MB-13X-CPEs	3	5.6	0.55	0.998 / 5	0.999 / 5
	5	5.4	0.61	0.998 / 5	0.998 / 6
	7	5.5	0.69	0.992 / 5	0.993 / 6
	8	5.5	0.72	0.996 / 5	0.999 / 5
	9	4.9	0.79	0.989 / 5	0.999 / 5
MG-13X-CPEs	3	6.6	0.82	0.986 / 5	0.978 / 7
	5	3.5	0.90	0.991 / 5	0.990 / 7
	6	2.9	0.80	0.993 / 6	0.986 / 8

Hydrogen peroxide electroreduction studies were performed by cyclic voltammetry on MB-13X-CPEs and MG-13X-CPEs immersed in H_2O_2 solutions of different concentrations (phosphate buffer, pH 7) (see Figure 4 for MB-13X-CPEs). In the presence of H_2O_2 an enhancement of the cathodic currents and a small peak potential shift towards negative direction with the increase of H_2O_2 concentration were observed. The electrocatalytic efficiency, estimated as the ratio, at an applied potential of -400 mV *vs.* Ag|AgCl/KCl$_{sat}$, in phosphate buffer pH 7, was 0.55 for MG-13X-CPEs and 0.10 for MB-13X-CPEs.

$$\frac{(I_{peak})_{[H_2O_2]=3mM} - (I_{peak})_{[H_2O_2]=0}}{(I_{peak})_{[H_2O_2]=0}}$$

The slight difference between the electrocatalytic activity of the two electrodes suggests that the acceptor group -NO_2 existing in the MG molecule enhances the electrocatalytic efficiency of this mediator.

Batch amperometric measurements at constant applied potential (-400 mV *vs.* Ag|AgCl/KCl_{sat}) proved that both MB-13X-CPEs and MG-13X-CPEs work well as H_2O_2 amperometric sensors (Figure 5), as suggested by the analytical parameters presented in Table 4.

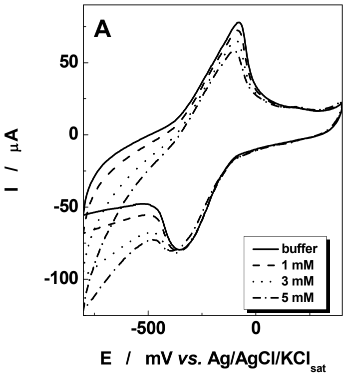


Figure 4. Cyclic voltammograms obtained at MB-13X-CPEs, in the absence and in the presence of H_2O_2. Experimental conditions: potential scan rate, 10 mV s^{-1}; starting potential, -800 mV *vs.* Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.0.

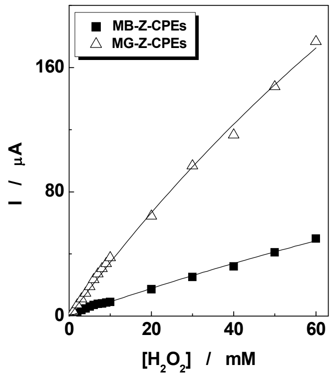


Figure 5. Calibration curves for H_2O_2 at MB-Z-CPEs and MG-13X-CPEs. Experimental conditions: applied potential, -400 mV *vs.* Ag|AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer, pH 6.0.

Table 4. Electroanalytical parameters corresponding to MB-13X-CPEs and MG-13X-CPEs modified electrodes. Experimental conditions: as in Figure 5.

Electrode	pH	Detection limit (mM)	Linear domain (M)	Sensitivity* (mA/M)	R / N
MB-13X-CPEs	6	0.13	$10^{-4} - 3\cdot10^{-1}$	1.20	0.991 / 8
	7	0.79	$8\cdot10^{-4} - 10^{-1}$	1.80	0.986 / 15
MG-13X-CPEs	6	0.42	$4\cdot10^{-4} - 2\cdot10^{-1}$	3.90	0.999 / 17
	7	0.60	$6\cdot10^{-4} - 1$	2.00	0.995 / 20

*calculated as the slope of calibration curve

The best detection limit (for a signal to noise ratio of 3) was obtained for MB-13X-CPEs in phosphate buffer pH 6 and that obtained for MG-13X-CPEs is better than that already reported by using a natural zeolitic volcanic tuff (natural X type mesoporous clinoptilolyte) [10]. In all cases the response time < 20 s.

The higher sensitivity of MG-13X-CPEs as compared with that of MB-13X-CPEs for H_2O_2 detection is in accordance with the better electrocatalytic effect of the MG-13X-CPEs, even if they exhibit smaller k_s values than MB-13X-CPEs.

CONCLUSIONS

Modified electrodes with electrocatalytic activity toward H_2O_2 reduction were obtained by Methylene Blue and Methylene Green adsorption on a synthetic zeolite (molecular sieves 13X, Aldrich), followed by their incorporation in carbon paste. The characteristics of the voltammetric response of MB-13X-CPEs and MG-13X-CPES (ΔEp of 90 and 46 mV, respectively and I_{pa}/I_{pc} of ~ 1) pointed out to a quasi-reversible, surface confined redox process in both cases.

The observed differences between the electrochemical behavior of MB-13X-CPEs and MG-13X-CPEs (the standard formal potentials, the effect of pH on $E^{0'}$ and the magnitude of the rate constants for heterogeneous electron transfer) as well as the electrocatalytic activity for H_2O_2 reduction can be explained in terms of mediator structure. The MG-13X-CPEs present a better sensitivity and electrocatalytic efficiency, but its $E^{0'}$ is not pH independent as in the case of MB-13X-CPEs.

Concluding, both investigated modified electrodes showed moderate catalytic efficiency towards H_2O_2 reduction and a relatively low limit of detection (0.13 mM for MB-13X-CPEs and 0.42 mM for MG-13X-CPEs, pH 6).

EXPERIMENTAL SECTION

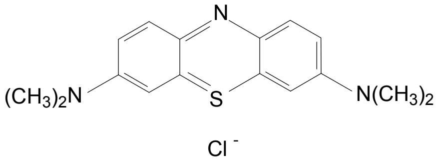
Chemicals

Methylene Blue (MB) and Methylene Green (MG) (Schemes 1 and 2), graphite powder and paraffin oil were purchased from Fluka (Buchs, Switzerland).

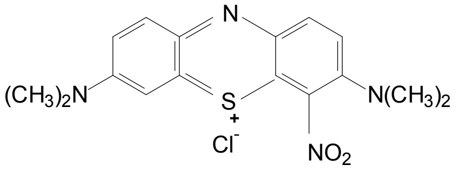
The 13X type zeolite, $1Na_2O:1Al_2O_3:2.8\pm0.2\ SiO_2 \times H_2O$ (particle size, 3-5μ; pore diameter, 10 Å; specific surface area 548.69 m^2/g; bulk density 480.55 kg/m^3; Si/Al ratio 1.5) was purchased from Aldrich (Germany).

Hydrogen peroxide, $K_2HPO_4\cdot2H_2O$ and $KH_2PO_4\cdot H_2O$ were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade and used as received.

The supporting electrolyte was a 0.1 M phosphate buffer solution. The pH was adjusted in the interval 1-9 using appropriate H_3PO_4 or NaOH solutions.



Scheme 1



Scheme 2

Electrode preparation

50 ml of a 0.001 % (w/v) MB or MG solution in water were shaken (3 days) with 50 mg zeolite. The modified zeolite was filtered, washed and dried. 25 mg of the modified zeolite were mixed with 25 mg graphite powder and 10 µl paraffin oil in order to obtain the modified carbon paste electrodes (MB-13X-CPEs and MG-13X-CPEs).

The preparation of MB-13X-CPEs and MG-13X-CPEs was reproducible when the experimental conditions and variables were maintained constant during the preparation period. The current response of the electrodes did not change significantly by storing them in air for several months.

Electrochemical measurements

Electrochemical experiments were carried out using a typical three-electrode electrochemical cell. The modified carbon paste electrode was used as working electrode, a platinum ring as counter electrode and an Ag|AgCl/KCl$_{sat}$ or SCE as reference electrodes.

Cyclic voltammetry experiments were performed on a PC-controlled electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, The Netherlands).

Batch amperometric measurements at different H_2O_2 concentrations were carried out at an applied potential of -400 mV *vs.* Ag|AgCl/KCl$_{sat}$, under magnetic stirring, using 0.1 M phosphate buffer solution (pH 7) as supporting electrolyte. The current-time data were collected using the above-mentioned electrochemical analyzer.

For each electrode, the surface coverage (Γ, mol cm^{-2}) was estimated from the under peak areas, recorded during the cyclic voltammetry (CV) measurements at low potential scan rate ($v \leq 10$ mV s^{-1}) [14] and considering the number of transferred electrons equal to 2 [15,16].

The experimental results are the average of at least 3 identically prepared electrodes, if not otherwise mentioned.

ACKNOWLEDGMENTS

Financial support from CNCSIS (Project ID_512) is gratefully acknowledged.

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